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Final Report

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Principal Investigator: Prof. J.M. Dyke
Dept. of Chemistry
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Southampton SO9 5NH
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19961129 076

Title: Photoelectron and Chemielectron Spectroscopy of Metal Oxides of Atmospheric Importance

Products of the gas-phase reactions M + $\rm N_2O$ and M + $\rm O_3$, where M=Na or K, have been investigated with u.v. photoelectron spectroscopy and the observed bands have been assigned with the assistance of results from ab initio molecular orbital calculations.

For the M + N₂O reactions, the observed products were MO + N₂. Measurement of the photoelectron bands associated with the metal monoxide, MO, allowed determination of the first adiabatic ionization energies (AIEs) of NaO and KO. The values obtained were AIE [NaO(X² Π)] = (7.1 ± 0.1) eV and AIE [KO(X² Π)] = (6.9 ± 0.1) eV. A similar study of the Li + N₂O reaction gave AIE [LiO(X² Π)] = (7.6 ± 0.2) eV.

The reactions M + 0_3 with M = Na or K, were observed to give M0 + 0_2 as the major reaction products. However, for each reaction a band was observed which was assigned to the first ionization energy of the secondary reaction product, M0₂. From the spectra obtained, the first adiabatic ionization energies of Na0₂ and K0₂ were measured as

AIE
$$[NaO_2(X^2A_2)] = (6.2 \pm 0.2)$$
 eV and
AIE $[KO_2(X^2A_2)] = (5.7 \pm 0.1)$ eV.

For both the M + N₂O and M + O₃ reactions, production of MO $A^2\Sigma^+$ was found to be favoured relative to production of the MO $X^2\Pi$ state, a result which has important implications in understanding the sodium night-glow in the mesosphere.

The ionization energy values determined in this work allow determination of ground state ionic dissociation energies. For example, for NaO⁺ and KO⁺ in their ground states, D_o has been derived as (0.60 ± 0.31) and (0.15 ± 0.14) eV respectively.

Reaction enthalpies can also be derived from the thermodynamic values derived in this work, for ion-molecule reactions of the type

$$MO + O_2^+ \rightarrow MO^+ + O_2$$
 (1)

For example for M = Na, ΔH_1 and ΔH_2 can be derived as -(4.98 \pm 0.11) and (0.23 \pm 0.44) eV respectively.

Work performed under this part of the contract, involving the study of Group I metals with oxidants, has been written up for publication and will soon be submitted to Journal of Chemical Physics. A preprint of this work is enclosed.

As part of an on-going experimental programme in chemiionization using chemielectron and chemiion spectroscopy, the ionization chamber of an electron spectrometer has been modified to allow ions and electrons to be sampled from the <u>same</u> reaction cell under a given set of experimental conditions simply by choosing the sign and magnitude of the extraction voltage on the cell. This experimental arrangement has been used to study the reaction of the group II metals (calcium, strontium and barium) with the oxidants $O_2(X^3\Sigma_g^-)$, $O_2(a^1\Delta_g)$ and $O(^3P)$. The results have been interpreted in terms of a simple thermodynamic model that is consistent with these reactions proceeding via long lived collision intermediates. The electron energy distributions have been interpreted in terms of a simple potential energy model, and the possibility

of the inclusion of an associative ionization reaction into a kinetic model of metal chemistry in the upper atmosphere has been considered. This work will soon be written up for publication.

Taking the Ba + $O_2(X^3\Sigma_g^-)$, Ba + $O_2(a^1\Delta_g)$ and Ba + $O(^3P)$ reactions as examples, the electron energy distributions and ions seen in the Ba + $O_2(X^3\Sigma_g^-)$ case can be interpreted in terms of the following processes:

$$Ba + O_2(X^3\Sigma_g^-) \rightarrow BaO_2^* \qquad \dots$$
 (3)

$$BaO_2^* + Ba \rightarrow Ba_2O_2^+ + e^-$$
 (4)

Adding $O_2(a^1\Delta_g)$ to the Ba + $O_2(X^3\Sigma_g^-)$ reaction mixture reduces the ion and electron yield by removing Ba atoms via the neutral reaction

Chemiionization can, however, occur via

$$Ba0^* + Ba \rightarrow Ba_20^+ + e^-$$
 (5)

On adding $O(^{3}P)$ to the system, BaO is produced via

which then undergoes chemiionization via reaction (5)

The new apparatus proved very useful in distinguishing between primary and secondary ions via the saturation current method, and in associating a given primary ion to an observed chemielectron band. The high kinetic energy offsets of the experimental chemielectron bands were used to estimate the exothermicities of the observed chemiionization reactions. Negative ion formation, a competing process to electron production in chemiionization, has also been investigated for the Group II metal plus oxidant reactions and in each case negative ion production has been found to be a minor channel.

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Southampton SO9 5NH,	UK			
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